

Particle-hole cumulant approach for inelastic losses in x-ray spectra

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Inelastic losses in core level x-ray spectra arise from many-body excitations, leading to broadening and damping as well as satellite peaks in x-ray photoemission (XPS) and x-ray absorption (XAS) spectra. Here we present a practical approach for calculating these losses based on a cumulant representation of the particle-hole Green's function, a quasi-boson approximation, and a partition of the cumulant into extrinsic, intrinsic and interference terms. The intrinsic losses are calculated using real-time, time-dependent density functional theory while the extrinsic losses are obtained from the GW approximation of the photo-electron self-energy and the interference terms are approximated. These effects are included in the spectra using a convolution with an energy dependent particle-hole spectral function. The approach elucidates the nature of the spectral functions in XPS and XAS and explains the significant cancellation between extrinsic and intrinsic losses. Edge-singularity effects in metals are also accounted for. Illustrative results are presented for the XPS and XAS for both weakly and more correlated systems.

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I. INTRODUCTION

Inelastic losses in x-ray spectra have long been of interest. These losses arise from electronic correlations, reflecting the coupling of electrons and holes to excitations of the system, such as plasmons and electron-hole pairs. Besides broadening and damping, they lead to additional features in the spectra that are not captured by the quasi-particle approximation. For example, in x-ray photoemission spectra (XPS) they correspond to satellites beyond the main quasi-particle peak and a reduction in main-peak intensity. As a result, conventional theories of x-ray spectra are usually only semi-quantitative. Two classes of losses have been identified: i) *intrinsic* losses which arise from excitations due to the sudden creation of a core hole, including shake-up, shake-off, and charge-transfer excitations; and ii) *extrinsic* losses, which arise from similar excitations during the propagation of the photo-electron. The extrinsic losses are often approximated in terms of the inelastic mean free path which is related to the imaginary part of the electron self-energy Σ .^{1,2} Interference effects have also been discussed, both formally and using approximate models.³⁻⁵

Surprisingly, inelastic losses in x-ray absorption spectra (XAS) are typically smaller than one might expect, as theoretical estimates of the intrinsic losses alone are typically about 30% of the main quasi-particle peak, even in weakly correlated systems.³ Moreover, losses due to satellites in XAS are almost always neglected in practical calculations, ranging from independent-particle to the Bethe-Salpeter Equation (BSE).⁶⁻⁸ Their neglect at low energies is often justified on the basis of the adiabatic approximation, and is often rationalized on the belief that the error is small or only contributes a smooth background, e.g. the many-body amplitude factor S_0^2 in XAS.⁹ The resolution of this paradox lies in the effect of the interference terms, as both classes of losses in-

volve similar excitations with couplings of opposite sign and tend to cancel.³ While it has been argued that this cancellation is perfect at threshold, at least for plasmon excitations,³ we find that it is generally incomplete, e.g., for the case of charge-transfer satellites. Another reason for their neglect is the computational difficulty of first principles of these losses, since various attempts ranging from plasmon pole models,⁵ configuration interaction (CI),¹⁰ multiplets,¹¹ to dynamical mean-field theory¹² have had only mixed success.

The aim of this work is twofold in an effort to address these issues: first we develop a formal approach based on a generalization of the cumulant Green's function (CG) that includes intrinsic and extrinsic losses and interference terms; and second we develop practical approximations for these losses which are applicable both to weakly-correlated and some *d*- and *f*-electron materials. In contrast to the Dyson equation for the one-particle Green's function $g = g^0 + g^0 \Sigma g$, the CG is based on an exponential representation in the time-domain $g(t) = g^0(t) e^{C(t)}$, where $g^0(t)$ is the non-interacting Green's function and $C(t)$ is the cumulant. This expansion is closely related to the linked-cluster theorem and has various uses in theoretical physics. Its applications to spectra were significantly developed by Hedin and collaborators,^{3,13} and a new derivation for the one-particle Green's function based on a functional differential equation has recently been developed.^{14,15} While no more demanding computationally than Hedin's GW approximation for the self-energy Σ , the CG has successfully explained satellite effects in the XPS of weakly correlated systems,¹⁴⁻¹⁷ while the GW approximation usually overestimates the satellite position and strength. Applications of cumulant methods to correlated materials based on the quasi-boson method³ and on dynamical mean-field theory,¹² have also been proposed.

Despite the above successes, the single-particle Green's

function alone is inadequate to describe x-ray spectra, which involves the simultaneous creation of both a particle and a hole. Instead, our generalization here is an analogous exponential representation of the “particle-hole Green’s function” $G_K(t) = G_K^0(t)e^{\tilde{C}_K(t)}$, where $\tilde{C}_K(t)$ is calculated to second order in the couplings to the excitations in the system. The structure of G_K is related to the effective Green’s function for x-ray spectra introduced by Campbell et al.⁵ (CHRB) transformed to the time-domain (see Appendix A). Here $K = (c, k)$ labels the transition from a given core-level $|c\rangle$ to a photoelectron state $|k\rangle$. A formal derivation of a related cumulant model for the 2-particle Green’s function has recently been introduced by Zhou et al.¹⁵ The real-time representation of $G_K(t)$ considerably simplifies the theory, and leads directly to an expression for the many-body XAS $\mu(\omega)$ at photon energy $\hbar\omega$ as a convolution of the spectrum calculated in the presence of a static core hole with an effective particle-hole spectral function $A_K(\omega)$

$$\mu(\omega) = \sum_k \int d\omega' A_K(\omega') \mu_K^0(\omega - \omega'). \quad (1)$$

Here $\mu_K^0(\omega)$ is the independent-particle XAS calculated in the presence of a core-hole, and $A_K(\omega) = -(1/\pi)\text{Im} G_K(\omega)$. A similar convolution – Eq. (49) in Ref. [5] – over the XAS fine structure $\chi_K(\omega)$ yields the many-body reduction factor S_0^2 in the XAS fine structure. Effects of thermal vibrations and disorder can be included implicitly in μ^0 and χ_K ¹⁸ by averaging over the structural variations. Convolutions related to that in Eq. (1) have also been used to incorporate inelastic losses in the XPS photocurrent $J_k(\omega)$.^{3,4,19}

Inelastic losses beyond the independent-particle approximation are embedded in the cumulant $\tilde{C}_K(t)$. Partitioning the cumulant into intrinsic, extrinsic, and interference terms then facilitates practical calculations beyond simple models. The factorization of the particle-hole Green’s function G_K implicit in the cumulant representation is analogous to that in the classic treatment of the x-ray edge singularities by Nozières and de Dominicis.²⁰ Likewise, our cumulant treatment also accounts for edge-singularities from low-energy particle-hole excitations in metals, as shown below.

The remainder of this paper is as follows. Sec. II. describes our theoretical approach including the treatment of edge-singularity effects, while Sec. III. contains applications to x-ray spectra for transition metals and charge-transfer satellites. Finally Sec. IV. contains a summary and conclusions.

II. THEORY

A. Particle-hole Green’s function

A detailed treatment of inelastic losses in core-level XAS is given by Campbell et al.,⁵ starting from the for-

mal expression

$$\mu(\omega) = -\frac{1}{\pi} \text{Im} \left\langle \Psi_0 \left| \Delta^\dagger \frac{1}{\omega - H + i\delta} \Delta \right| \Psi_0 \right\rangle. \quad (2)$$

This starting point is equivalent to the many-body Fermi golden rule, where H is the total Hamiltonian which includes electron-electron interactions, $|\Psi_0\rangle$ the N -particle ground state of the system (including valence electrons and ion cores) with energy E_0 , and $\Delta = \sum_k \langle k|d|c\rangle c_k^\dagger c_c + hc$ is the dipole operator coupling the photon to the electronic system. Unless otherwise specified we use atomic units, $m = |e| = \hbar = 1$, and temperature is assumed to be zero. The system is then partitioned into three subsystems, a single core-level $|c\rangle$, the valence electrons $|\Phi\rangle$, and the photoelectron levels $|k\rangle$; the core-hole is eliminated using a canonical transformation. This partition then leads to an expression for the XAS in terms of an effective single particle Green’s function $\tilde{G}(\omega)$ (see Appendix A) which is a contraction of the “particle-hole” Green’s function $G_K(\omega)$ for a discrete core state $|c\rangle$,

$$\mu(\omega) = -\frac{1}{\pi} \text{Im} \langle c|d^\dagger P \tilde{G}(\omega) P d|c\rangle, \quad (3)$$

where $\epsilon_k = \epsilon_c + \hbar\omega$, and $P = \sum_{k>k_F} |k\rangle\langle k|$ is the projection operator onto unoccupied levels of the initial state. As in CHRB, \tilde{G}_K is approximated using a quasi-boson model Hamiltonian in which the three subsystems are represented in terms of a core-hole and a photoelectron coupled to a set of bosonic excitations, e.g., plasmons, particle-hole excitations, etc., keeping all terms to second order in the couplings. Next we introduce a cumulant ansatz for \tilde{G}_K

$$\tilde{G}_K(t) = \tilde{G}_K^0(t) e^{\tilde{C}_K(t)}, \quad (4)$$

where $\tilde{G}_K^0(t) = g_c^0(t)g_k^0(t)$, and $g_c^0(t)$ and $g_k^0(t)$ are the bare core-hole and photoelectron Green’s functions, respectively, the latter being calculated in the presence of the core-hole. The generalized cumulant $\tilde{C}_K(t)$ is determined (Appendix A) by transforming Eq. (32) of CHRB to the time-domain, and matching the leading terms in powers of the quasi-boson coupling constants,

$$\tilde{C}_K(t) = \int d\omega \gamma_K(\omega) (e^{i\omega t} - i\omega t - 1). \quad (5)$$

This ansatz is similar to that derived by Zhou et al.,¹⁵ where G_K is the 2-particle Green’s function of the Bethe-Salpeter equation. However, the cumulants differ in technical details. The Landau representation²¹ of Eq. (5) ensures that the particle-hole spectral function

$$\tilde{A}_K(\omega) = -\frac{1}{\pi} \text{Im} \int dt e^{i\omega t} \tilde{G}_K^0(t) e^{\tilde{C}_K(t)} \quad (6)$$

remains normalized with an invariant centroid. Thus the effect of the bosonic excitations is a transfer of spectral weight from the main peak to the satellites while the overall strength is conserved. Note that lifetime broadening

due to the photoelectron interactions is included naturally, while core-hole lifetime effects can be treated by adding a damping term, $-\Gamma_c|t|$, to the cumulant. In addition to describing the excitation spectrum, the cumulant formalism simplifies the calculation of both the quasi-particle peak shift (or relaxation energy) Δ_E and the net quasiparticle weight (or renormalization constant) Z_K in terms of the kernel $\gamma_K(\omega) = \beta_K(\omega)/\omega^2$,³

$$Z_K = e^{-a_K}, \quad (7)$$

$$a_K = \int \frac{\beta_K(\omega)}{\omega^2} d\omega, \quad (8)$$

$$\Delta_E = \int_0^\infty \frac{\beta_K(\omega)}{\omega} d\omega. \quad (9)$$

The excitation spectrum $\beta_K(\omega)$ for XAS is implicit in the particle-hole cumulant $C_K(t)$, and hence the structure of $\gamma_K(\omega)$. This structure can be understood formally in terms of the *fluctuation potentials* or oscillator strength amplitudes V^q that couple electron and hole states to boson excitations q with energies ω_q ^{3-5,22} (see Appendix A). Formally the fluctuation potentials can be obtained by diagonalizing the screened coulomb potential $W = \epsilon^{-1}v$. As an illustrative example, the fluctuation potential for plasmons of momentum q in the homogeneous electron gas is $V^q = [v_q\omega_p^2/2\omega_q]^{1/2} \exp(i\mathbf{q} \cdot \mathbf{r})$, where $v_q = 4\pi/q^2$ is the bare Coulomb interaction. If recoil due to plasmon dispersion is ignored, $\gamma_K(\omega)$ can be expressed as a perfect square,

$$\gamma_K(\omega) = \sum_q \left| V_{\mathbf{k}\mathbf{k}+\mathbf{q}}^q g_{\mathbf{k}+\mathbf{q}}^0(\omega - \omega_q) - \frac{V_{cc}^q}{\omega_q} \right|^2 \delta(\omega - \omega_q). \quad (10)$$

This representation is similar to that in the treatment of inelastic losses in XPS,^{3,4,22} where the fluctuation potentials V^q are discussed in detail. Unfortunately, this form does not seem to be computationally useful except in simple models, due to the non-local character of the interference terms. Moreover, its general validity is questionable. Thus instead, we partition γ_K , and hence $C_K(t)$, into intrinsic (c), extrinsic (k), and interference terms (ck), respectively, i.e.,

$$\tilde{\gamma}_K(\omega) = \gamma_c(\omega) + \gamma_k(\omega) + \gamma_{ck}(\omega), \quad (11)$$

$$\tilde{C}_K(t) = C_c(t) + C_k(t) + C_{ck}. \quad (12)$$

The amplitudes a_K and shifts Δ_E can also be split into intrinsic, extrinsic, and interference contributions. The intrinsic and extrinsic parts of Δ_E are formally equivalent to those of the GW approximation, while the interference term tends to reduce the shift. Similarly, the renormalization constant can be related to derivatives of the self-energy at the quasiparticle energies, i.e., $Z_k = \exp(-a_k)$ where $a_k = d\Sigma_k/d\omega + d\Sigma_c/d\omega - a_{ck}$, and again the interference terms reduce many-body effects, restoring weight to the quasiparticle peak. Note that in using a final state rule (or static BSE) approximation as the starting point in Eq. (1), this shift is already taken into account. In

order to avoid double counting and considering the approximations used for the interference terms, we subtract this shift in our final results.

If interference is neglected, the particle-hole Green's function would be simply a product of the core-hole Green's function $g_c(t) = g_c^0(t)e^{C_c(t)}$ and the damped final state Green's function in the presence of a core hole $\tilde{g}_k(t) = \tilde{g}_k^0(t)e^{C_k(t)}$. This approximation implies that the intrinsic and extrinsic losses are independent and additive. However this yields XAS satellite strengths that are generally too large. Thus the interference terms are usually essential; they provide an energy dependence which tends to cancel the extrinsic and intrinsic losses near threshold, due to the opposite signs of the hole and photoelectron charges, while at very high energies only the intrinsic losses remain. This phenomena is characterized as an adiabatic to sudden transition. It is used to justify the adiabatic approximation and the usual neglect of inelastic losses near threshold, i.e., well below the characteristic excitation energy ω_p .

In any case, the above partition of the cumulant $\tilde{C}_K(t)$ permits independent treatments of the various terms. This is advantageous computationally as the physics of the intrinsic and extrinsic losses can differ significantly. Here we treat the intrinsic losses with the cumulant $C_c(t)$ for the core-hole Green's function using a real-space, real-time method of Kas et al. (KVRC),²³ as described below. This local approach was found to account well for charge-transfer satellites in the XPS of transition metal oxides. In contrast, the extrinsic losses are treated using the cumulant approximation $C_k(t)$ for the photoelectron Green's function. Finally the interference terms $C_{ck}(t)$ are approximated, e.g., with an interpolation formula. We note, however, that the partition of the cumulant is somewhat arbitrary, and can be tailored for computational purposes. For example, CHRB lump the quasi-particle part of the cumulant into the damped particle Green's function in the presence of a core hole, $\tilde{g}_k(t) = g_k'^0(t) \exp[C_k^{qp}(t)]$, so that the net spectral function only contains the satellite contributions. The full many body XAS $\mu(\omega)$ can then be expressed as a convolution of an independent particle XAS with a spectral function as in Eq. (1), where $\mu^0(\omega)$ is the independent particle XAS calculated in the presence of a core hole.

B. Intrinsic Losses

The intrinsic losses are given by the leading factors in $G_K(t)$, which correspond to a cumulant representation of the core-hole Green's function,

$$g_c(t) = i\theta(t)e^{-i\epsilon_c t + C_c(t)}, \quad (13)$$

where $\theta(t)$ is the unit step function. In terms of the fluctuation potentials, the intrinsic excitation spectrum $\gamma_c(\omega) \equiv \beta_c(\omega)/\omega^2$ can be expressed as $\beta_c(\omega) = \sum_q |V_{cc}^q|^2 \delta(\omega - \omega_q)$. Physically V^q/ω_q can be interpreted

as a shake-up amplitude, and from first order perturbation theory, is equivalent to a many-body overlap integral between the ground state and the shake-up excited state $|Kq\rangle$ with a boson in state q and a core hole in level $|c\rangle$.⁵

The localized nature of a deep core-hole in x-ray spectra has led us to consider a real-space, real-time approach for the intrinsic cumulant $C_c(t)$ introduced by KVRC,²³ which is not limited to small clusters. Our treatment is based on a time-dependent density functional theory formalism (RT-TDDFT) inspired by that of Bertsch and Yabana²⁴ for optical response. Such methods are advantageous for calculations of density response, since they are quantitative yet require little computational effort beyond successive applications of Kohn-Sham DFT in the time-evolution of the system. RT-TDDFT has been successfully applied both to linear and non-linear optical response.^{25–28} The approach has also been applied to calculate the quasiparticle contribution $\mu^{qp}(\omega)$ in Eq. (1) to core-level x-ray absorption spectra, using a time-correlation approach that ignores satellites.²⁹

We will refer to $C_c(t)$ as the *Langreth cumulant*,³⁰ since a similar formalism was introduced to calculate edge singularities in electron gas models of deep-core x-ray spectra, following the classic treatment of Nozières and de Dominicis.²⁰ Transforming Langreth’s approach^{22,30} to real-space, $C_c(t)$ can be approximated to second order in the core-hole potential by

$$C_c(t) = \int d\omega \beta_c(\omega) \frac{e^{i\omega t} - i\omega t - 1}{\omega^2}, \quad (14)$$

$$\beta_c(\omega) = \int d^3r d^3r' V^*(\mathbf{r}) V(\mathbf{r}') \text{Im}[\chi(\mathbf{r}, \mathbf{r}', \omega)]. \quad (15)$$

The time dependence $[\exp(i\omega t) - i\omega t - 1]/\omega^2$ arises from the transient core-hole potential, which turns on at time $t = 0$ and then off at time t . Here $V(\mathbf{r})$ is the bare core-hole potential, and the response function,

$$\chi(\mathbf{r}, \mathbf{r}', \omega) = i \int dt e^{i\omega t} \langle \hat{\rho}(\mathbf{r}, t) \hat{\rho}(\mathbf{r}', 0) \rangle, \quad (16)$$

is equivalent to the dynamic structure factor which is directly related to the local density-density correlation function $\langle \hat{\rho}(\mathbf{r}, t) \hat{\rho}(\mathbf{r}', 0) \rangle$, where $\hat{\rho}(\mathbf{r}, t)$ is the density operator.

In more detail, our approach is as follows: $\beta_c(\omega)$ is obtained from the Fourier transform of the “core-response” function $\Delta_c(t)$ using the relations²³

$$\beta_c(\omega) = \omega \text{Re} \int dt e^{-i\omega t} \Delta_c(t), \quad (17)$$

$$\Delta_c(t) = \int d^3r V(\vec{r}) \delta\rho(\vec{r}, t), \quad (18)$$

where $\delta\rho(\vec{r}, t)$ is the change in electron density from equilibrium due to the core-hole perturbation, and $V(\vec{r})$ is the potential due to the presence of the core-hole.²³ This function $\Delta_c(t)$ is computed using RT-TDDFT via a modified version of the SIESTA framework.³¹

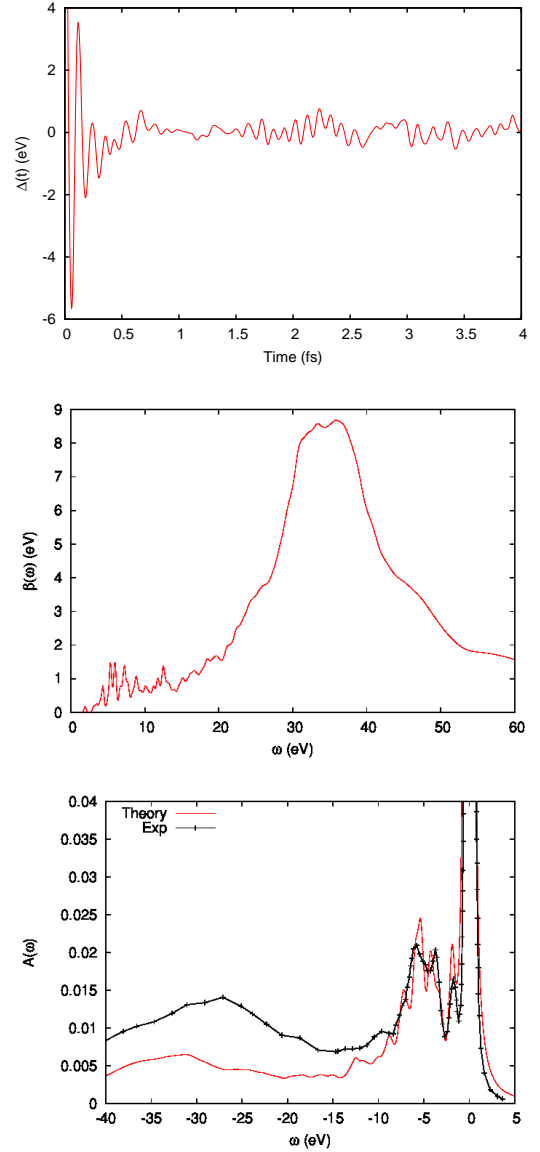


FIG. 1: (Color online) a) (top) The core response function $\Delta(t)$; b) (middle) $\beta_c(\omega)$ for C_{60} , and c) (bottom) Theoretical core-level spectral function of C_{60} compared to experimental 1s XPS.³²

The normalized core-hole spectral function $A_c(\omega)$, which characterizes the distribution of intrinsic excitations, is then obtained from the imaginary part of $g_c(\omega)$ in frequency space,

$$A_c(\omega) = -\frac{1}{\pi} \text{Im} \int dt e^{i\omega t} g_c(t). \quad (19)$$

This procedure is illustrated here for the fullerene molecule C_{60} in the gas phase, and results for $\Delta(t)$ and $\beta_c(\omega)$ are shown (top and middle respectively) in Fig. 1, along with a comparison of the spectral function with experimental XPS results. Additional details for the case of C_{60} will be published elsewhere.³³ As an illustration of

the theory, we present calculations of the core-hole spectral function $A_c(\omega)$. As discussed below, A_c is closely related to the core XPS, and is in good agreement with the experimental spectrum, apart from a smooth background term, and a mismatch of the high binding energy peak in the experiment at about -27 eV, and in the theory at about -31 eV. This energy shift could be due to a variety of factors including the use of a local basis set or the approximate kernel used in the TDDFT. For this example we have not included extrinsic and interference effects, which are expected to increase the weight of the plasmon peak relative to the lower energy peaks.

As discussed in Ref. [3], the XPS photocurrent $J_k(\omega)$ can be approximated by $A_c(\omega)$ when the energy dependence of the matrix elements can be neglected, apart from a smooth background,

$$J_k(\omega) = |M_{ck}|^2 A_c(\omega) \approx A_c(\omega), \quad (20)$$

where M_{ck} is the dipole transition element. The extrinsic and interference terms may also be important, although in monoatomic weakly correlated systems, they mostly affect size of the satellites and not their shape.^{4,14} For quantitative calculations, a particle-hole spectral function $\tilde{A}_K(\omega)$ tailored for the XPS photocurrent is needed. This spectral function differs from that in XAS due to the differences in boundary conditions, such as the effects of the surface on the fluctuation potentials. In particular, in XPS, the finite inelastic mean free path of the photoelectron limits the depth from which electrons can reach the surface (and detector). Photoelectrons originating deeper in the material, i.e., with longer mean free paths, have larger probabilities of creating excitations. On the other hand, small mean free paths are associated with larger couplings, and thus the two effects compete. For a deep hole coupled to ideal plasmons or bosons, the cumulant representation of $g_c(t)$ given by Eq. (14) and (15) is exact.³⁰ It can be shown that this approximation is equivalent to the decoupling approximation of Ref. [14]. However, corrections to the 2nd order approximation for the cumulant will generally affect the structure of higher order satellites.

C. Edge singularities

For metallic systems, edge singularities have been predicted due to existence of particle-hole excitations at zero frequency.^{20,30} In this case $\beta_c(\omega) \sim \omega$ at low frequency, and the usual description of the quasiparticle peak becomes problematical, because the quasiparticle weight is strictly zero, a phenomenon known as the Anderson orthogonality catastrophe.³⁴ Instead the spectral function, and hence the threshold peak in XPS is predicted to have a power-law singularity $A_c(\omega) \sim \omega^{\alpha-1}$, as discussed in many works.^{20,30,34,35} Anderson, and later Nozieres and de Dominicis derived the exponent $\alpha = 2\Sigma_l(2l+1)(\delta_l/\pi)^2$ in terms of the phase shifts δ_l at the Fermi energy induced by the core-hole potential. Subsequently Langreth

related α to the low frequency behavior of the loss function,

$$\alpha = \sum_{q < 2q_F} \frac{|v_q|^2 N(\epsilon_F)}{qv_F |\epsilon(\mathbf{q}, 0)|^2}, \quad (21)$$

where $N(\epsilon_F)$ is the density of states at the Fermi level, v_F is the Fermi velocity, and v_q is the Fourier transform of the core-hole potential to momentum space. This power-law singularity corresponds to a logarithmic behavior of the cumulant in the long time limit $C(t) \rightarrow \ln(t^{-\alpha})$.

Here we have reinvestigated this singular behavior within the cumulant formalism. We generalize the quasiparticle line-shape to an asymmetric form that includes a power-law singularity, analogous to that of Doniach and Sunjic.³⁵ To do this we further partition the core-hole excitation spectrum $\beta_c(\omega)$ into “particle-hole” and “plasmon” contributions, where the particle-hole contributions only contribute at low frequencies and give the part of the excitation spectrum $\beta_{ph}(\omega)$ which is linear in frequency. This linear part responsible for the logarithmic divergence of the cumulant in the long time limit, and hence the singular behavior at threshold. We therefore redefine the main peak in terms of the normalized

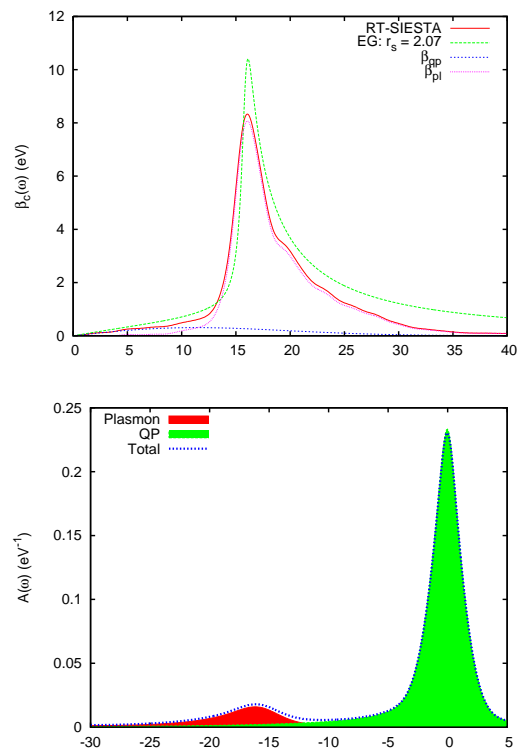


FIG. 2: Results of the calculated core excitation spectrum (top) of Al using the real-time TDDFT method compared to that of an electron gas with $r_s = 2.07$. The model particle hole part and plasmon parts are also shown. The bottom portion shows the total spectral function (dashed) along with partition into the main (green filled) and satellite (red filled) parts.

spectral function A_{ph} resulting from the “particle-hole” contribution of the excitation spectrum $\beta_{ph}(\omega)$, which is defined with an *ad hoc* exponential damping factor to enforce normalizability of the spectral function

$$\beta_{ph}(\omega) = \alpha \omega e^{-\omega/\omega_p}. \quad (22)$$

The exponent α corresponds to the linear coefficient at low frequencies and ω_p is the plasmon frequency. The precise nature of the damping is not important as it does not effect the edge singularity, and the net excitation spectrum is conserved by setting the plasmon part as $\beta_{pl}(\omega) = \beta(\omega) - \beta_{ph}(\omega)$. Substituting this form into Eq. (14) for the particle-hole cumulant gives

$$C_{ph}(t) = -i\alpha\omega_p t - \alpha \ln(1 - i\omega_p t). \quad (23)$$

The main peak of the core-hole Green’s function and the associated spectral function are then

$$g_{ph}(t) = -ie^{-i(\epsilon_c + \alpha\omega_p)t - \alpha \ln(1 - i\omega_p t)}, \quad (24)$$

$$A_{ph}(\omega) = e^{-a_{pl}} \frac{e^{-\tilde{\omega}/\omega_p}}{\Gamma(\alpha)} \frac{\omega_p^{-\alpha}}{\tilde{\omega}^{1-\alpha}}, \quad (25)$$

where $\tilde{\omega} = \omega - \epsilon_c - \alpha\omega_p$ is the frequency relative to threshold. This representation has the correct behavior at long times as well as at $t = 0$, where the cumulant must vanish to preserve normalization. The weight of the quasiparticle spectral function, i.e., the generalized renormalization constant) is given by the plasmon-part $Z = e^{-a_{pl}}$, which is reduced from unity due to the high energy (e.g. plasmon) excitations,

$$a_{pl} = \int d\omega \frac{\beta_{pl}(\omega)}{\omega^2}, \quad (26)$$

$$\beta_{pl}(\omega) = \beta(\omega) - \beta_{ph}(\omega).$$

As an example, we show the separation of the particle-hole and plasmon peaks for fcc Al in Fig. 2 (bottom).

We note that this edge-singularity correction only appears in the intrinsic spectral function in metals; there is generally no contribution from the extrinsic losses for photoelectron states k far above threshold. However, for XAS an additional Mahan edge singularity factor

$$\tilde{\mu}(\omega) \sim \omega^{-2\delta_l/\pi}, \quad (27)$$

appears in the dipole-matrix elements due to the non-orthogonality of the one-particle levels with and without the core hole.^{5,20} Even in insulators, one may expect a non-singular enhancement factor given by Eq. (27), with the threshold Fermi energy set at mid-gap. In contrast the main peak in the extrinsic spectral function $A_k(\omega)$ has an asymmetric Fano line shape, as discussed by Aryasetiawan et al.¹³ Finally, we note that the finite lifetimes of the core-hole and photoelectron will broaden the observed edge singularity.

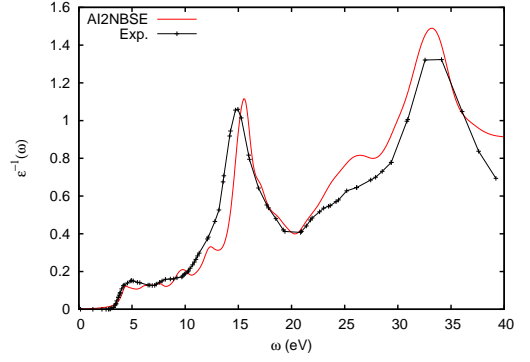


FIG. 3: (Color online) Theoretical loss function of CeO₂ compared with experimental results.³⁶ Note that the first major peak at ≈ 15 eV corresponds very well with the high binding energy satellite in the XPS, whereas the low energy satellite has no corresponding peak in the loss function.

D. Extrinsic Losses

Our treatment of extrinsic losses in the cumulant $C_k(t)$ is based on the GW approximation to the cumulant, as discussed by Hedin and others for the one-particle Green’s function, and leads to a Landau form similar to that for intrinsic losses. The difference is that the kernel is given by

$$\beta_k(\omega) = \frac{1}{\pi} |\text{Im} \Sigma_k(\omega + \epsilon_k)|, \quad (28)$$

where $\Sigma_k(\omega)$ is the electron self-energy calculated in the GW approximation.^{15,37} Formally the GW self-energy can be expressed in terms of fluctuation potentials as $\Sigma(\omega) = \Sigma_q V^q \tilde{g}(\omega - \omega_q) V^q$. In contrast to the CG, the spectral function from the GW approximation only contains single boson excitations. In this work we use the efficient many-pole model self-energy² to calculate the kernel. The model is based on a representation of the dielectric function in the screened coulomb interaction $W = \epsilon^{-1}v$ in terms of plasmon-like excitations, and matches to a zero momentum-transfer loss function $L(\omega)$,

$$L(\omega) = -\text{Im} \epsilon^{-1}(\omega). \quad (29)$$

In this work $L(\omega)$ is calculated via the first-principles code AI2NBSE, which solves the GW/Bethe-Salpeter equation for valence excitations.³⁸ As an example, we show the calculated loss function for CeO₂ compared to experiment in Fig. 3. The GW excitation spectrum in the cumulant from $\text{Im} \Sigma_k$ is then given by the MPSE model as a sum of plasmon pole self-energies,

$$\text{Im} \Sigma_k(\omega) = \sum_i g_i \text{Im} \Sigma_k^i(\omega; \omega_i), \quad (30)$$

where $\Sigma^i(\omega, \omega_i)$ is the the plasmon pole self-energy evaluated with plasmon frequency ω_i , and g_i is the associated weight from the pole representation of the loss function.

E. Interference Terms

The calculation of the interference terms poses a number of technical difficulties, especially in the treatment of recoil. Although various approximations have been introduced, including plasmon-pole models and semi-classical approximations,^{3,5,22,39} none is as yet fully satisfactory, and can lead to negative spectral weight in some cases. On the other hand, one expects physically that the kernel $\beta_K(\omega)$, like β_c and β_k , should be positive definite. Another complication with the interference terms is that the exchange of a boson between the photoelectron and hole should be associated with a change in photoelectron state, i.e., $k \rightarrow k + q$. Only if this is neglected (at least partially) can the particle-hole Green's function be considered diagonal, so that Eq. (1) is strictly valid (see Appendix A). This approximation is not expected to capture all excitonic effects well, which is why we use a starting point that includes the static interaction and screening of the core-hole, and apply the convolution to incorporate non-adiabatic effects. In terms of fluctuation potentials the interference contribution is given by the cross-terms in Eq. (10)

$$\gamma_{ck}(\omega) = -2 \sum_{\mathbf{q}} \frac{V_{\mathbf{k}\mathbf{k}+\mathbf{q}}^{\mathbf{q}} V_{cc}^{\mathbf{q}*}}{\omega_{\mathbf{q}} \omega_{\mathbf{k}\mathbf{q}}} \delta(\omega - \omega_{\mathbf{k}\mathbf{q}}). \quad (31)$$

Here $\omega_{\mathbf{k}\mathbf{q}} = \omega_{\mathbf{q}} + \epsilon_{\mathbf{k}-\mathbf{q}} - \epsilon_{\mathbf{k}}$ is the excitation energy including recoil. Various approximations can be used in practical calculations. For example, the recoil effects can be approximated by neglecting the cross terms in $\omega_{\mathbf{k}\mathbf{q}}$, i.e., averaging over all directions $\hat{\mathbf{q}}$, so that $\omega_{\mathbf{k}\mathbf{q}} \approx \omega_{\mathbf{q}} + (1/2)q^2$.⁴⁰ We find that for the plasmon pole model, neglecting recoil altogether is a reasonable approximation for k near k_F , although some of the integrals become ill defined at large k when recoil is neglected. A similar recoil approximation was used in deriving the cumulant expansion for the one-particle Green's function.⁴⁰ We find that for the plasmon pole model, this approximation is reasonable for k near k_F , although some of the integrals may become ill defined at large k when recoil is neglected. As an alternative, both the positive-definiteness of the total kernel, and qualitative behavior of the interference terms can be enforced by approximating the interference term as

$$\beta_{ck}(\omega) = -2\lambda \sqrt{\beta_c(\omega)\beta_k(\omega)}. \quad (32)$$

where λ is an adjustable parameter. Here we compare only calculations with $\lambda = 1$ or $\lambda = 0$. This *ad hoc* interpolation model ignores the phases in the interference amplitudes but preserves the correct limiting behavior: $\lambda = 1$ gives the maximum possible interference, while interference is neglected when $\lambda = 0$ and vanishes if either $\beta_c(\omega)$ or $\beta_k(\omega)$ is zero. We have also verified that this form gives a good approximation to the satellite weight when compared to the interference term within the plasmon pole approximation [Eq. (A9) in Appendix A].

In order to assess the quality of the above approximation, we calculated the interference within the plasmon

pole model near the Fermi momentum, which is of particular importance for XANES. First, we used the interpolation model above, and second, an approximation which neglects recoil (see Appendix A). Fig. 4 shows that these two approximations are nearly identical near k_F .

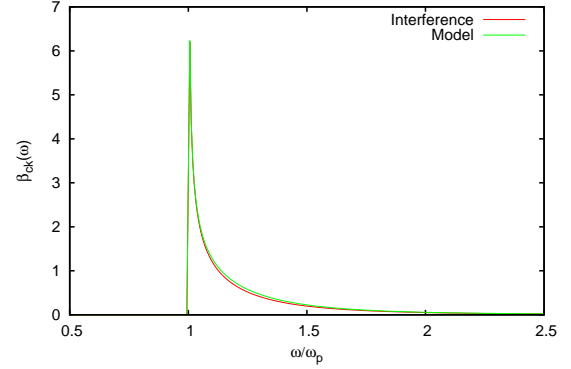


FIG. 4: (color online) Comparison of calculated interference term $\beta_{ck}(\omega)$ (red) with the interpolation model given by Eq. (32) (green) for $k = k_F$. Both were calculated using the plasmon pole approximation and the recoil approximation detailed in Appendix A.

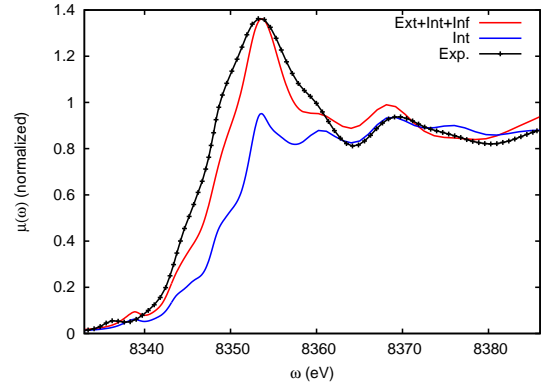


FIG. 5: (color online) Ni K-edge XAS spectrum for NiO calculated with intrinsic losses alone (blue), and all losses (red), compared to experiment (crosses).¹⁹

The importance of interference effects in XAS is demonstrated in Fig. 5, which shows a comparison between experiment and calculations of the XAS of NiO with only intrinsic losses (blue) and with all losses (red). Clearly the results agree remarkably well with experiment. They also compare well with previous work,^{19,41} although in those approaches the experimental XPS was used to approximate the spectral function, and interference effects were assumed to cancel the high energy plasmon entirely. For this example, the amplitude of the core-hole potential was adjusted in order to achieve reasonable agreement with satellite intensity in the XPS.

III. X-RAY SPECTRA

Finally in this section we present illustrative results of our approach for the XPS and XAS for a variety of materials. The single particle XAS spectra were calculated using the FEFF9 code,¹⁸ which was then convolved with the spectral function derived above.

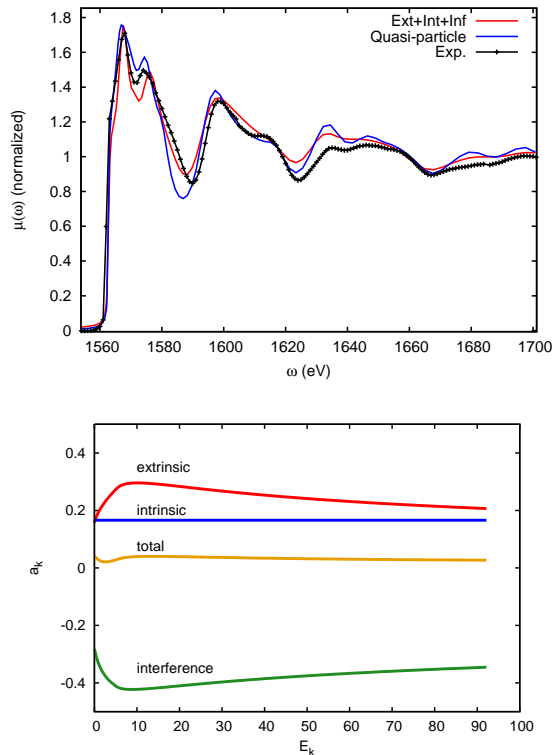


FIG. 6: (Color online) (top) Theoretical Al K-edge XAS spectrum compared to the quasi-particle theory in this work and experimental data;⁴² and (bottom) total satellite weight a_k for Al and different contributions as a function of the particle energy E_k . Note that the total satellite strength has the expected structure, being small at threshold and exhibiting significant cancellation among the various contributions.

A. K-edge Al

As a first example, we show the experimental XAS for fcc Al metal compared to the calculated results including the cumulant convolution, and those of the single particle calculation (Fig. 6 top). Both calculations both agree fairly well with experiment, although the single particle spectrum does not contain enough broadening at about 1590 eV, where the dip is too large. The figure (bottom panel) also shows the separate contributions from the intrinsic, extrinsic, and interference satellites. Note that the interference terms nearly completely cancel the weight of the extrinsic and intrinsic satellites, and return

that weight to the quasiparticle peak, showing that in this case, the adiabatic approximation is reasonable.

B. Elemental transition metals

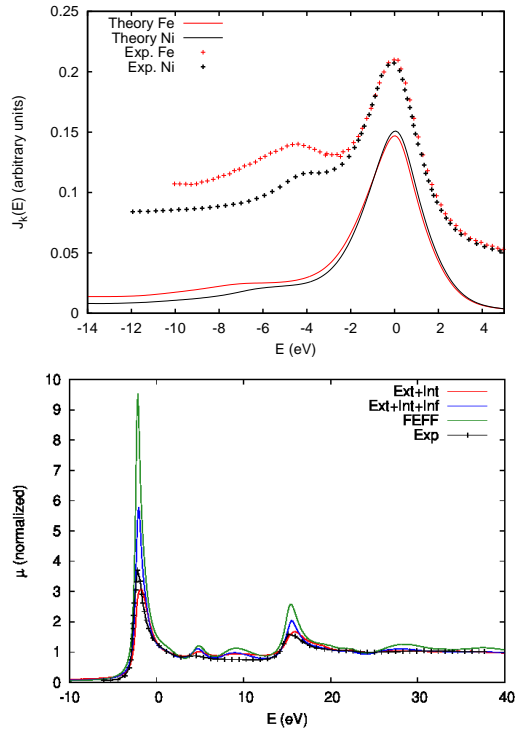


FIG. 7: (Color online) Calculated spectral function of Fe, and Ni compared to experimental Ni 1s and Fe 3s XPS data (top).^{43,44} The calculated Ni K-edge XANES is also compared to experiment (bottom).⁴⁵

As an application of the theory to d -electron materials, we present results for the core-hole spectral function and photocurrent of elemental transition metals Fe and Ni from Eq. (20) in Fig. 7. For these systems a 6 eV satellite observed in some experimental spectra has been of great interest, but it's origin has been controversial, especially for Ni. Interestingly the RT-TDDFT approach also yields satellites around 6 eV; however, their amplitude is smaller than that observed in experiment. In addition, the experimental XPS data for Ni shows a satellite closer to 4 eV. This energy/amplitude mismatch is also apparent in the comparison of theory and experiment in Fe. However, the qualitative differences between theory and experiment are consistent, where the satellite moves toward the main peak with decreased amplitude going from Fe to Ni.

Next we use the particle-hole spectral function to calculate the XAS using the convolution in Eq. (1). As Fig. 7 indicates, the effect of the satellites generally adds to the asymmetry of the edge peak, leading better agreement with experiment than the single particle spectrum.

In this case, ignoring interference effects ($\lambda = 0$) seems to be a reasonable approximation, although this agreement may be due in part to the neglect of multiplet effects that mix the edges.

C. Charge-transfer satellites

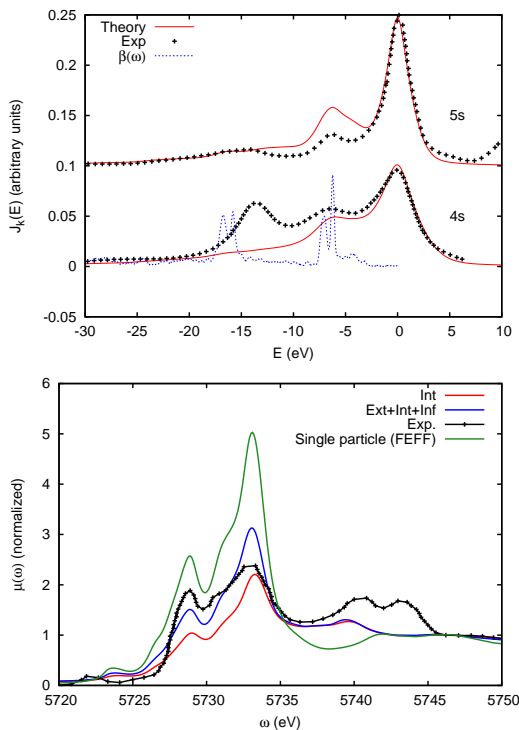


FIG. 8: (Color online) Theoretical Ce 4s and 5s XPS of CeO_2 compared with experiment⁴⁶ (top) and similarly the Ce L_3 XAS spectrum (bottom) at various levels of approximation, also compared to experiment.⁴⁷

Charge-transfer (CT) excitations are particularly strong in transition metal oxides, and have been the subject of numerous investigations.^{19,23,48} Here we discuss the application of our particle-hole cumulant approach to CT satellites, namely the f -electron system CeO_2 , again following the treatment of the intrinsic losses in XPS by KVR. The top plot in Fig. 8 shows the core-hole spectral function compared to the experimental Ce 4s and 5s XPS of CeO_2 . The agreement in peak position is reasonable, although the qualitative change in satellite amplitudes in going from the 4s to 5s hole is not reproduced. There could be several reasons for this discrepancy: first, our present calculations ignore the shape of the core-state, and thus the core-hole potential may not be accurate; and second – and possibly more important for the case of CeO_2 – the core-hole potential is assumed to be a static coulomb potential and exchange is ignored. Third, the 5s states are treated as core states in the calculation, and should probably be promoted into the valence for this system. Finally, frustrated Auger

configurations can also play a role in the spectrum, but are not treated here.¹⁰ Fig. 8 (bottom) shows our calculations of the XAS of CeO_2 calculated at various levels of theory and compared with experiment. Interestingly the agreement with experiment is quite reasonable with only intrinsic losses, suggesting that extrinsic losses and interference have a minor effect on the XAS. Consequently these CT systems represent cases where the cancellation of the intrinsic and extrinsic losses is generally incomplete at threshold, and that intrinsic losses are essential for a quantitative treatment. This is supported by investigations of CT systems using the 3-state model of Lee, Hedin, and Gunnarsson,^{19,41,48} where the sudden limit is reached at relatively low energies, and that the interference is in fact constructive near threshold. This constructive interference is missing in our model of interference (at least with $\lambda = 1$), and may be one reason for some missing amplitude in our CT excitation in CeO_2 .

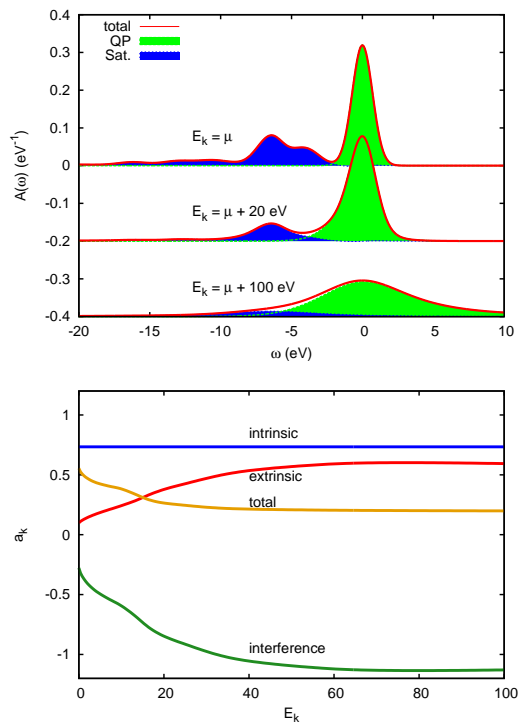


FIG. 9: (Color online) For reference the particle-hole spectral function $\tilde{A}_K(\omega)$ for CeO_2 (top) and the satellite weights of the individual contributions (bottom) are also given.

IV. CONCLUSIONS

We have developed both the theory and a practical approach for calculating inelastic losses due to intrinsic, extrinsic and interference effects in x-ray spectra within a generalized particle-hole cumulant expansion, and a partition of the cumulant into extrinsic, intrinsic and interference contributions. These losses are included in the

spectra in terms of a convolution with a particle-hole spectral function that accounts for their energy dependence. The cumulant approach simplifies the formalism and facilitates practical calculations. Here the core-hole cumulant is calculated via a real-time real-space approach, while an efficient many-pole model self-energy is used to obtain the extrinsic part. Interference effects are approximated using an interpolation model. This model avoids the complications of recoil effect which can lead to a number of technical problems such as unphysical negative spectral weight at some energies. The approach is complementary to, and can be used to correct various methods for calculating XAS and XPS that ignore inelastic losses and satellites e.g., in a post-processing step. The cumulant theory also elucidates both their behavior and the differences between the spectral functions for XAS and XPS which may be important to their interpretation. In contrast to the relatively sharp features of independent particle spectral function for the ground state, the particle-hole spectral function exhibits significant breadth and asymmetry of both the quasi-particle peak and the satellite contributions well above the Fermi energy. The cumulant approach can also account for edge singularities in the spectrum. Physically, the treatment of inelastic losses here is analogous to an “excitonic polaron,” i.e., the interaction of the particle-hole created in photoexcitation with the density fluctuations produced by the particle-hole system. This is in contrast to the “electronic polaron” described by the GW approximation,³ where the single-particle excitations arise from the generally stronger density fluctuations due to a core-hole or a photoelectron. For the L-edge XAS of Fe and Ni, the spectral function reduces the whiteness significantly and increases the asymmetry of the peak, bringing the theoretical curve closer to experiment, and giving good agreement, especially in Ni. However, there is missing weight at roughly 5-7 eV, indicating that the strength of the satellites in this region is underestimated with the current approximation. As in CHRB, we find that interference effects play a large role in reducing the effects of many-body excitations, especially in XAS. However, in general, we find the cancellation to be incomplete, especially in charge-transfer systems, where the intrinsic satellites are dominant. For these cases the inclusion of both interference terms and extrinsic losses are usually essential to provide a quantitative treatment of the near edge spectrum. Finally, although effects of thermal vibrations are not discussed in detail here, they can be folded into the calculation of the single particle spectrum $\mu^0(\omega)$. These effects can be approximated via the use of Debye-Waller factors as in the real-space multiple scattering code FEFF9,^{18,49} by convolving with an effective quasiparticle spectral function,³³ or by performing a configurational average over MD snapshots. The effects of phonons on the satellite structure is expected to be rather weak, and is in many cases obscured by the large core-hole lifetime, but can also be treated via cumulant methods.^{50,51}

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Appendix A: Inelastic losses XAS

Here we briefly summarize the derivation of the generalized particle-hole cumulant. We start with the treatment in CHRB⁵ where the many-body XAS is given by

$$\mu(\omega) = -\frac{1}{\pi} \text{Im} \langle c | d^\dagger P g_{\text{eff}}(\omega + E_c) P d | c \rangle. \quad (\text{A1})$$

effective Green’s function g_{eff} can be conveniently expressed in terms of the fluctuation potentials $V^{\mathbf{q}}$ which diagonalize the dielectric response,

$$\text{Im } W(\mathbf{r}, \mathbf{r}', \omega) = \sum_{\mathbf{q}} V^{\mathbf{q}}(\mathbf{r}) V^{*\mathbf{q}}(\mathbf{r}') \delta(\omega - \omega_{\mathbf{q}}). \quad (\text{A2})$$

The effective Green’s function then becomes

$$g_{\text{eff}}(\omega) = e^{-a} \left[\tilde{g}(\omega) + \sum_{\mathbf{q}} \left| \frac{V_{cc}^{\mathbf{q}}}{\omega_{\mathbf{q}}} \right|^2 \tilde{g}(\omega - \omega_{\mathbf{q}}) - 2 \sum_{\mathbf{q}} \frac{V_{cc}^{\mathbf{q}}}{\omega_{\mathbf{q}}} \tilde{g}(\omega - \omega_{\mathbf{q}}) V^{\mathbf{q}} \tilde{g}(\omega) \right], \quad (\text{A3})$$

where $\tilde{g}(\omega)$ is the photoelectron Green’s function in the presence of the core-hole including extrinsic interactions and $a = \sum_{\mathbf{q}} |V_{cc}^{\mathbf{q}}/\omega_{\mathbf{q}}|^2$. expression simplifies considerably in the time domain. for example the second term which characterizes the satellite contribution from intrinsic losses as $\sum_{\mathbf{q}} |V_{cc}^{\mathbf{q}}/\omega_{\mathbf{q}}|^2 \exp(i\omega_{\mathbf{q}}t)$. Similarly if we now express g_{eff} to second order in the fluctuation potentials which are implicit in the definition of $g(\omega)$, we obtain

$$g_{\text{eff}}(\omega) = g^0(\omega) + \left[\sum_{\mathbf{q}} g^0(\omega) V^{\mathbf{q}} g^0(\omega - \omega_{\mathbf{q}}) V^{\mathbf{q}} g^0(\omega) + \sum_{\mathbf{q}} \left| \frac{V_{cc}^{\mathbf{q}}}{\omega_{\mathbf{q}}} \right|^2 g^0(\omega - \omega_{\mathbf{q}}) - 2 \sum_{\mathbf{q}} \frac{V_{cc}^{\mathbf{q}}}{\omega_{\mathbf{q}}} g^0(\omega - \omega_{\mathbf{q}}) V^{\mathbf{q}} g^0(\omega) \right]. \quad (\text{A4})$$

Now we can follow the procedure of Gunnarson to derive a second order cumulant approximation for the effective Green’s function in the time domain which has the structure of a particle-hole Green’s function,

$$G_K(t) = g_c^0(t) g_k^0(t) e^{C_K(t)} \quad (\text{A5})$$

$$C_K(t) = \int d\omega \gamma_K(\omega) (e^{i\omega t} - i\omega t - 1)$$

$$\gamma_K(\omega) = \gamma_k(\omega) + \gamma_c(\omega) + \gamma_{kc}(\omega). \quad (\text{A6})$$

The kernels γ_c and γ_k of the intrinsic and extrinsic cumulants are given by

$$\begin{aligned}\gamma_c(\omega) &= \sum_{\mathbf{q}} \frac{|V_{cc}^{\mathbf{q}}|^2}{\omega_{\mathbf{q}}^2} \delta(\omega - \omega_{\mathbf{q}}), \\ \gamma_k(\omega) &= \sum_{\mathbf{q}} \frac{|V_{\mathbf{k}\mathbf{k}+\mathbf{q}}^{\mathbf{q}}|^2}{\omega_{\mathbf{k}\mathbf{q}}^2} \delta(\omega - \omega_{\mathbf{k}\mathbf{q}}) \\ &= \frac{|\text{Im}\Sigma_{\mathbf{k}}(\omega + E_{\mathbf{k}})|}{\pi\omega^2}.\end{aligned}\quad (\text{A7})$$

The interference term can be derived similarly, although a further approximation of constant matrix elements must be made, namely $\langle k|d|c\rangle = \langle k+q|d|c\rangle$. This yields the interference kernel

$$\gamma_{kc}(\omega) = -2 \sum_{\mathbf{q}} \frac{V_{cc}^{\mathbf{q}} V_{\mathbf{k}\mathbf{k}+\mathbf{q}}^{\mathbf{q}}}{\omega \omega_{\mathbf{k}\mathbf{q}}} \delta(\omega - \omega_{\mathbf{k}\mathbf{q}}), \quad (\text{A8})$$

where $\omega_{\mathbf{k}\mathbf{q}} = \omega_{\mathbf{q}} + E_{\mathbf{k}+\mathbf{q}} - E_{\mathbf{k}}$.

As a concrete example, we illustrate the result with the plasmon pole approximation for the dielectric function. In that case the fluctuation potentials are plane waves, $V^{\mathbf{q}}(\mathbf{r}) = V_0^{\mathbf{q}} \exp(\mathbf{k} \cdot \mathbf{r})$. Thus we have $V_{cc}^{\mathbf{q}} = V_0^{\mathbf{q}}$ and $V_{\mathbf{k}\mathbf{k}'}^{\mathbf{q}} = v_0^{\mathbf{q}} \delta_{\mathbf{k}', \mathbf{k}+\mathbf{q}}$. The integrals over \mathbf{q} can be performed, to find explicit expressions for the contributions to $\gamma_K(\omega)$, however, we find that this solution is plagued

by unphysical behavior such as negative spectral density. If we instead neglect recoil ($\epsilon_{\mathbf{k}+\mathbf{q}} \approx \epsilon_{\mathbf{k}}$) in the delta functions, we can then write the complete excitation spectrum as a perfect square, which will ensure a positive definite result. In that case we find

$$\begin{aligned}\gamma_k(\omega) &= \frac{\omega_p^2 \theta(\omega - \omega_p)}{\pi \omega \sqrt{2(\omega - \omega_p)}} \\ &\quad \times \frac{1}{[(2\omega - \omega_p)^2 - 2k^2(\omega - \omega_p)]}, \\ \gamma_c(\omega) &= \frac{\omega_p^2 \theta(\omega - \omega_p)}{\pi \sqrt{2(\omega - \omega_p)} \omega^3}, \\ \gamma_{kc}(\omega) &= \frac{\omega_p^2 \theta(\omega - \omega_p)}{4\pi k \omega^2 (\omega - \omega_p)} \\ &\quad \times \ln \left[\frac{2\omega - \omega_p + k \sqrt{2(\omega - \omega_p)}}{2\omega - \omega_p - k \sqrt{2(\omega - \omega_p)}} \right],\end{aligned}\quad (\text{A9})$$

where for simplicity we have taken the plasmon dispersion to be $\omega_q = \omega_p + 1/2q^2$ and $V_0^{\mathbf{q}} = [v_q \omega_p^2 / 2\omega_q]^{1/2}$. Unfortunately, these expressions are only valid for low photoelectron momentum k , since the integrals are ill defined for large k when recoil is neglected. However, we use them only to evaluate our approximation for the interference term in reference to XANES calculations, where the photoelectron momentum is relatively low.

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- ¹ L. Hedin, Phys. Rev. **139** (1965).
 - ² J. J. Kas, A. P. Sorini, M. P. Prange, L. W. Cambell, J. A. Soininen, and J. J. Rehr, Phys. Rev. B **76**, 195116 (2007).
 - ³ L. Hedin, J. Phys.: Condens. Matter **11**, R489 (1999).
 - ⁴ L. Hedin, J. Michiels, and J. Inglesfield, Phys. Rev. B **58**, 15565 (1998).
 - ⁵ L. Campbell, L. Hedin, J. J. Rehr, and W. Bardyszewski, Phys. Rev. B **65**, 064107 (2002).
 - ⁶ L. Triguero, L. Pettersson, and H. Ågren, J. Phys. Chem. A **102**, 10599 (1998).
 - ⁷ J. Vinson, J. J. Rehr, J. J. Kas, and E. L. Shirley, Phys. Rev. B **83**, 115106 (2011).
 - ⁸ P. Puschnig and C. Ambrosch-Draxl, Phys. Rev. B **66**, 165105 (2002).
 - ⁹ J. J. Rehr, E. A. Stern, R. L. Martin, and E. R. Davidson, Phys. Rev. B **17**, 560 (1978).
 - ¹⁰ P. Bagus, C. Nelin, E. Ilton, M. Baron, H. Abbott, E. Primorac, H. Kühlenbeck, S. Shaikhutdinov, and H.-J. Freund, Chem. Phys. Lett. **487**, 237 (2010).
 - ¹¹ F. de Groot and A. Kotani, *Core Level Spectroscopy of Solids* (CRC Press, 2008).
 - ¹² M. Casula, A. Rubtsov, and S. Biermann, Phys. Rev. B **85**, 035115 (2012).
 - ¹³ F. Aryasetiawan, L. Hedin, and K. Karlsson, Phys. Rev. Lett. **77**, 2268 (1996).
 - ¹⁴ M. Guzzo, G. Lani, F. Sottile, P. Romaniello, M. Gatti, J. J. Kas, J. J. Rehr, M. G. Silly, F. Sirotti, and L. Reining, Phys. Rev. Lett. **107**, 166401 (2011).
 - ¹⁵ J. Zhou, J. Kas, L. Sponza, I. Reshetnyak, M. Guzzo, C. Giorgetti, M. Gatti, F. Sottile, J. Rehr, and L. Reining, J. Chem. Phys. **143** (2015).
 - ¹⁶ J. Lischner, D. Vigil-Fowler, and S. G. Louie, Phys. Rev. Lett. **110**, 146801 (2013).
 - ¹⁷ F. Caruso and F. Giustino, Phys. Rev. B **92**, 045123 (2015).
 - ¹⁸ J. J. Rehr, J. J. Kas, M. P. Prange, A. P. Sorini, Y. Takimoto, and F. Vila, C. R. Phys. **10** (2009).
 - ¹⁹ M. Calandra, J. P. Rueff, C. Gougoussis, D. Céolin, M. Gorgoi, S. Benedetti, P. Torelli, A. Shukla, D. Chandresris, and C. Brouder, Phys. Rev. B **86**, 165102 (2012).
 - ²⁰ P. Nozières and C. T. de Dominicis, Phys. Rev. **178**, 1097 (1969).
 - ²¹ L. Landau, J. Phys. USSR **8**, 201 (1944).
 - ²² W. Bardyszewski and L. Hedin, Phys. Scr. **32**, 439 (1985).
 - ²³ J. J. Kas, F. D. Vila, J. J. Rehr, and S. A. Chambers, Phys. Rev. B **91**, 121112 (2015).
 - ²⁴ K. Yabana and G. F. Bertsch, Phys. Rev. B **54**, 4484 (1996).
 - ²⁵ K. Yabana, T. Nakatsukasa, J.-I. Iwata, and G. F. Bertsch, Phys. Status Solidi B **243**, 1121 (2006).
 - ²⁶ Y. Takimoto, F. D. Vila, and J. J. Rehr, J. Chem. Phys. **127**, 154114 (2007).
 - ²⁷ F. D. Vila, D. A. Strubbe, Y. Takimoto, X. Andrade, A. Rubio, S. G. Louie, and J. J. Rehr, J. Chem. Phys. **133**, 034111 (2010).
 - ²⁸ T. Otake, K. Yabana, and J.-I. Iwata, J. Comput. Theory Nanosci **6**, 2545 (2009).
 - ²⁹ A. J. Lee, F. D. Vila, and J. J. Rehr, Phys. Rev. B **86**,

- 115107 (2012).
- ³⁰ D. C. Langreth, Phys. Rev. B **1**, 471 (1970).
 - ³¹ J. Soler, E. Artacho, J. Gale, A. Garcia, J. Junquera, P. Ordejón, and D. Sanchez-Portal, J. Phys.: Condens. Matter **14** (2002).
 - ³² J. Leiro, M. Heinonen, T. Laiho, and I. Batirev, J. Electron. Spectrosc. Relat. Phenom. **128**, 205 (2003).
 - ³³ E. L. Shirley, F. Fossard, K. Gilmore, G. Hug, J. J. Kas, J. J. Rehr, and F. D. Vila, unpublished.
 - ³⁴ P. W. Anderson, Phys. Rev. Lett. **18**, 1049 (1967).
 - ³⁵ S. Doniach and M. Sunjic, J. Phys. C (Solid State) **3**, 285 (1970).
 - ³⁶ F. Goubin, X. Rocquefelte, M.-H. Whangbo, Y. Montardi, R. Brec, and S. Jobic, Chem. Mater. **16**, 662 (2004).
 - ³⁷ J. J. Kas, J. J. Rehr, and L. Reining, Phys. Rev. B **90**, 085112 (2014).
 - ³⁸ H. M. Lawler, J. J. Rehr, F. Vila, S. D. Dalosto, E. L. Shirley, and Z. H. Levine, Phys. Rev. B **78**, 205108 (2008).
 - ³⁹ D. Sokcevic, M. Sunjik, and C. Fadley, Surf. Sci. **82**, 383 (1979).
 - ⁴⁰ L. Hedin, Phys. Scr. **21**, 477 (1980).
 - ⁴¹ E. Klevak, J. J. Kas, and J. J. Rehr, Phys. Rev. B **89**, 085123 (2014).
 - ⁴² P. Lagarde, private communication (1999).
 - ⁴³ O. Karis, S. Svensson, J. Rusz, P. M. Oppeneer, M. Gorgoi, F. Schäfers, W. Braun, W. Eberhardt, and N. Mårtensson, Phys. Rev. B **78**, 233105 (2008).
 - ⁴⁴ Z. Xu, Y. Liu, P. D. Johnson, B. Itchkawitz, K. Randall, J. Feldhaus, and A. Bradshaw, Phys. Rev. B **51**, 7912 (1995).
 - ⁴⁵ C. T. Chen, N. V. Smith, and F. Sette, Phys. Rev. B **43**, 6785 (1991).
 - ⁴⁶ P. Bagus, C. Nelin, E. Ilton, M. Baron, H. Abbott, E. Primorac, H. Kuhlenbeck, S. Shaikhutdinov, and H.-J. Freund, Chem. Phys. Lett. **487**, 237 (2010).
 - ⁴⁷ A. Kotani, K. O. Kvashnina, S. M. Butorin, and P. Glatzel, EPJ B **85**, 1 (2012).
 - ⁴⁸ J. D. Lee, O. Gunnarsson, and L. Hedin, Phys. Rev. B **60**, 8034 (1999).
 - ⁴⁹ F. D. Vila, J. J. Rehr, H. H. Rossner, and H. J. Krappe, Phys. Rev. B **76**, 014301 (2007).
 - ⁵⁰ S. M. Story, J. J. Kas, F. D. Vila, M. J. Verstraete, and J. J. Rehr, Phys. Rev. B **90**, 195135 (2014).
 - ⁵¹ O. Gunnarsson, V. Meden, and K. Schönhammer, Phys. Rev. B **50**, 10462 (1994).